This Page Is Inserted by IFW Operations and is not a part of the Official Record

BEST AVAILABLE IMAGES

Defective images within this document are accurate representations of the original documents submitted by the applicant.

Defects in the images may include (but are not limited to):

- BLACK BORDERS
- TEXT CUT OFF AT TOP, BOTTOM OR SIDES
- FADED TEXT
- ILLEGIBLE TEXT
- SKEWED/SLANTED IMAGES
- COLORED PHOTOS
- BLACK OR VERY BLACK AND WHITE DARK PHOTOS
- GRAY SCALE DOCUMENTS

IMAGES ARE BEST AVAILABLE COPY.

As rescanning documents will not correct images, please do not report the images to the Image Problem Mailbox.

*	्रक्षाचित्रं वेद्यांचा रेक्ट्र	, H								***	a nelle		74.73 M	
		- 1		A start				And P. Alex		ř (;		<i>i</i>		
50. 1				•					F					
i is											•			
						, see Fee sa								į
				*.			÷	,						
ji ser						3								, T
説 ひ は、・・・・・		·				**								•
\$ \$ 						194								ĺ
Spiles Chan														
						· · · · · · · · · · · · · · · · · · ·								
t :				•					× '		.			Silvery). _{Zy} ja
· · · · · · · · · · · · · · · · · · ·														· · · · · · · · · · · · · · · · · · ·
100 min (100)						* .		÷						#-1 **** ****
		•					•						. *	
				•										
2-2 2-3 1-4														
3.0		3	j.	رائو <u>اگر</u> اند	**							_ + 1	 	

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No
PCT/EP 02/10031

Patent document cited in search report		Publication date		Patent family member(s)	Publication date
EP 1008305	Α	14-06-2000	EP	1008305 A1	14-06-2000
			AU	3037500 A	26-06-2000
			BR	9907829 A	28-11-2000
			CA	2320363 A1	15-06-2000
			CN	1324215 T	28-11-2001
			WO	0033671 A2	15-06-2000
			EP	1056355 A2	06-12-2000
			JP	2002531110 T	24-09-2002
			NO	20003954 A	04-08-2000
			PL	343204 A1	30-07-2001

			S	· · · · · · · · · · · · · · · · · · ·	
349					
,					
	•	•			



Europäisches Patentamt

European Patent Office

Office européen des brevets



EP 1 008 305 A1 (11)

(12)

EUROPEAN PATENT APPLICATION

(43) Date of publication: 14.06.2000 Bulletin 2000/24 (51) Int. Cl.7: A23L 1/035, A23L 1/22, A23L 1/227, A23L 1/231

(21) Application number: 98123554.2

(22) Date of filing: 10.12.1998

(84) Designated Contracting States: AT BE CH CY DE DK ES FI FR GB GR IE IT LI LU MC NL PT SE Designated Extension States:

AL LT LV MK RO SI

(71) Applicant: SOCIETE DES PRODUITS NESTLE S.A. 1800 Vevey (CH)

(72) Inventors:

 Vauthey, Sylvain 1110 Morges (CH)

 Leser, Martin 1054 Morrens (CH)

 Milo, Christian 1006 Lausanne (CH)

(74) Representative: Thomas, Alain et al 55, avenue Nestlé 1800 Vevey (CH)

An aroma product comprising saturated C16 and C18 monoglycerides (54)

- The invention concerns an aroma product com-(57)prising flavoring compounds, obtainable through a process comprising:
- dissolving in water amino acids, peptides or hydrolized proteins and reducing sugars or dissolving in water aroma precursors,
- introducing in said solution a monoglyceride, which is a saturated compound in C16 and C18,
- heating the obtained mixture to have a mesomorphic phase structure or a microemulsion,
- maintaining said heating to develop flavoring compounds
- and cooling said mixture.

EP 1 008 305 A1

Description

10

15

[0001] The present invention concerns an aroma product comprising flavoring compounds and the use of said aroma product.

[0002] The Maillard reaction is well known in the food area as being a non enzymatic browning. This type of reaction is of primary importance in food industry since it is one of the most important routes to production of flavour, taste and color in cooked food. This type of reaction occurs in a mixture where amino acids together with reducing sugars are heated and react together to give a very broad range of compounds: this range can be as large as comprising near to 200 different compounds. In the food technology, it is already known to induce a Maillard reaction for the production of a certain range of aroma compounds. The US Patent No. 4'466'986 for example concerns a process for the production of a flavoring agent resembling in taste meat, fish or mushrooms, wherein a liquid protein hydrolysate is reacted with at least one monosaccharide by heating. The reaction is carried out in water. The problem with this type of reaction in purely aqueous medium is that firstly the yield of the reaction is not very high and secondly it is not possible to obtain a very broad range of aroma compounds.

[0003] Furthermore, it is possible to obtain through thermal degradation of aroma precursors flavor compounds. The problem with this type of reaction is the same as for the Maillard reaction, that is, firstly the yield of the thermal reaction is not very high and secondly it is not possible to obtain a very broad range of aroma compounds.

[0004] The aim of the present invention is to have the possibility of inducing a Maillard reaction or a degradation of aroma precursors, that is thermal reaction flavors, wherein the yield of the obtained aroma compounds is greater than in the aqueous phase and wherein the range of these compounds is larger. Furthermore, the obtained aroma product has an increased stability at room temperature.

[0005] The invention concerns an aroma product comprising flavoring compounds , obtainable through a process comprising :

- dissolving in water amino acids, peptides or hydrolized proteins and reducing sugars or dissolving in water aroma precursors,
 - introducing in said solution a monoglyceride, which is a saturated compound in C16 and C18,
 - heating the obtained mixture to have a mesomorphic phase structure or a microemulsion,
 - maintaining said heating to develop flavoring compounds
- 30 and cooling said mixture.

[0006] In the case of a mixture of amino acids, peptides or hydrolized proteins and reducing sugars, it is the Maillard reaction which takes place. In the case of aroma precursors, it is a thermal degradation which takes place.

[0007] The mesomorphic phase which is obtained is preferably a cubic phase.

[0008] It is known that cubic phase can be used to solubilize large amount of hydrophilic, hydrophobic and amphiphilic molecules without significantly changing the main rheological properties. Moreover, their inherent high viscosity, as well as a three-dimensional structure with well-defined water channels, makes cubic phases attractive as potential delivery system to provide sustained release of volatile compounds in air.

[0009] Instead of using the cubic phase to solubilize guest molecules, it has been found according to the present invention that flavoring compounds are directly generated in the mesophase. Thus, the cubic phases play the role of an active matrix where the aroma is created at a defined time in the final product by heating and then released in a controlled way. The cubic phases are an innovative tool to manage flavour generation pathways since this particular structure is able to compartmentalize and concentrate the potential precursors and final flavoring compounds.

[0010] It is important to use according to the invention a monoglyceride, which is substantially saturated and with a carbon chain between 16 and 18. The monoglyceride used is normally a 100 % saturated C16 compound or a 100 % saturated C18 compound or a mixture of both. It is also possible to work with a saturated monoglyceride comprising molecules outside this chain length, but in this case the amount of non-C16 or C18 compounds must not exceed 20 %. It is furthermore possible to have a certain amount of unsaturated compounds. As above mentioned, in this case the amount of unsaturated compounds must not exceed 20 %. All the percentages given in the present specification are in weight.

[0011] In the technique, it is known that a Maillard reaction takes place at a temperature comprised between 80 to 150 °C. By considering a phase diagram with different monoglycerides, it has been stated that the use of an unsaturated monoglyceride decreases the cubic to hexagonal phase transition temperature, which drops below 100 °C: so that it is not possible at such a temperature to induce a real efficient Maillard reaction. This is the reason why we use according to the present invention substantially saturated monoglyceride in C16 and/or C18. In this case, the phase diagram increases the cubic to hexagonal phase transition temperature to a range where an efficient Maillard reaction is induced. The cubic phase region occurs from about 80 to 120 °C.

[0012] In the case of a thermal degradation, the aroma precursors used are normally thiamine.

50

EP 1 008 305 A1

; '

[0013] The used monoglycerides are normally solid at room temperature. It is therefore necessary to dissolve said monoglycerides at a temperature around 60 °C in the solution of both types of the reaction compounds precursors.

[0014] One possible mechanism which leads to the remarkable rate enhancement is compartmentalization of the reactants (amino acids, peptides or hydrolyzed proteins and reducing sugars or aroma precursors) at the monoglyceride-water interface or close to it, thus inducing a concentration gradient. Therefore, due to locally high concentration of amino acids, peptides or hydrolyzed proteins and reducing sugars or aroma precursors, the chemical reactions are strongly accelerated leading to higher yields of key odorant molecules or even new volatile compounds which are normally not detected in bulk water.

[0015] The amino acids are taken in the group consisting of cystein, methionine, glycine, glutathione and and monosodium glutamate, the proteins in the group consisting of milk proteins, soy proteins, cereal proteins, vegetable proteins and meat proteins. The peptides are taken from the same group as the proteins or synthetized peptides.

[0016] The reducing sugars are taken in the group consisting of ribose, xylose, glucose, fructose, rhamnose and galacturonic acid.

[0017] By considering the phase diagram with the monoglyceride, which is the better for the high yield of flavoring compounds, it is preferred to have in the reaction mixture an amount of monoglyceride comprised between 60 and 80 %, an amount of amino acids, proteins, peptides and reducing sugars comprised between 0.1 and 5 % and an amount of aroma precursors comprised between 0.1 and 5 %, the remaining being water. The amount of water in the mixture is preferably around 20 %.

[0018] According to the invention, the heating of the mixture is carried out at a temperature comprised between 80 and 180 °C during 1 to 6 hours. Systems of the Maillard reaction are often studied at higher temperature (around 140-180 °C) and shorter time (10-20 minutes). It is preferred to carry out the heating at a temperature around 100 °C during 4 hours, because of the necessity to stay in the cubic phase region and to avoid the use of pressurizable reaction vessels.

[0019] During the Maillard reaction, the presence of the monoglyceride in the cubic phase allows the Maillard reaction compounds to be then encapsulated, in such a manner that said compounds have a controlled release.

[0020] It has been found that according to the invention, it is possible to obtain ten times more certain Maillard compounds.

[0021] For the thermal reaction of the aroma precursors, the heating is carried out at the same temperature range as for the Maillard reaction, that is between 80 and 180 °C during 1 to 6 hours.

[0022] There is no criticality in the cooling step. This cooling can be carried out at room temperature.

[0023] The present invention concerns further the use of the aroma product comprising flavoring compounds, wherein 0.1 to 5 % of the aroma product is mixed with a food taken in the group consisting of bouillons, soup sauces, gravies, pet food, snacks and canned food.

[0024] The mixing of the aroma product can be carried out by different ways. It is possible to add directly the aroma product in the food. It is also possible to prepare a dispersion in an aqueous medium and then make the mixing. Finally, it is possible to make a drying, by way of spray drying and then add a powder to the food.

[0025] The following of the specification is now made in relation with the example.

Example

30

[0026] 2 mmol of cysteine and 2 mmol of ribose were dissolved in 10 ml of phosphate buffer (0.5 mol/l) at pH 5.0. The cubic phase was prepared by introducing 1 g of this solution and 4 g of melted (60°C) monoglyceride (product of the Company Danisco sold under the trade mark Dimodan PV) into a Pyrex tube. After vigorous stirring, the tube was placed in an oil bath at 140 °C for 1 minute and stirred again to form an homogeneous cubic phase. Finally, the cubic phase was thermally treated for 4 hours at 100 °C.

[0027] This thermally treated sample is then compared with a reference comprising the same amount of the reactant, but without the monoglyceride: this reference is called aqueous system in the following of the specification.

[0028] The sensory properties of the reaction flavour of the aqueous system with that of the cubic phase were compared by an untrained technical sensory panel. The reaction carried out in the cubic phase was found to have an overall more intense flavour with a strong rubber, eggy, roast chicken-like aroma. The aroma of the aqueous reaction was evaluated after transforming the solution into a cubic phase system in order to have similar volatile-matrix interactions. This mixture was then described as weak in an aroma reminiscent of meat and lard with some burnt character.

[0029] The volatiles formed in the cubic phase compared to those in water were monitored by gas chromatography.

[0030] The following table gives the amount of products generated from the ribose and cysteine solubilized in the cubic phase and in the water system.

5

10

Component Cubic phase (µg) Water (µg) 2-Methyl-3-furanthiol (MFT) 18.4 n.d. 2-Methyl-3(2H)-furanone 36.7 13.1 **Furfural** 874.3 351.0 **Furfurylthiol** 12.0 trace 3-Mercapto-2-pentanone trace n.d. Norfuraneol 698.1 291.1

15

30

35

45

The present table shows drastic differences between the two samples indicating a much higher generation [0031] of sulfur compounds in the cubic system. The results show a significant increase in the concentration of furfurylthiol in the cubic phase compared to the water system in which only trace amounts were detected. At the same time, the potent odorant 2-methyl-3-furanthiol was only detected in the cubic phase system.

Besides MET also its potential precursors furfural and norfuraneol were favored in the cubic phase, being formed 2.5 fold higher amounts.

Claims

- 1. An aroma product comprising flavoring compounds , obtainable through a process comprising :
 - dissolving in water amino acids, peptides or hydrolized proteins and reducing sugars or dissolving in water

introducing in said solution a monoglyceride, which is a saturated compound in C16 and C18,

heating the obtained mixture to have a mesomorphic phase structure or a microemulsion, maintaining said heating to develop flavoring compounds

- and cooling said mixture.
- 2. An aroma product according to claim 1, wherein the mesomorphic phase is a cubic phase.
- An aroma product according to claims 1 or 2, wherein the amino acids are taken in the group consisting of cystein, methionine, glycine, glutathione and and monosodium glutamate, the proteins in the group consisting of milk proteins, soy proteins, cereal proteins, vegetable proteins and meat proteins.
- 4. An aroma product according to any of claims 1 to 3, wherein the sugars are taken in the group consisting of ribose, 40 xylose, glucose, fructose, rhamnose and galacturonic acid.
 - 5. An aroma product according to any of claims 1 to 4, wherein the monoglyceride is present in an amount comprised between 60 and 80 %, the amino acids, the proteins, the peptides and the sugars in an amount comprised between 1 and 5 % and the aroma precursors in an amount comprised between 0.1 and 5 %, the remaining being water.
 - 6. An aroma product according to any of claims 1 to 5, wherein the heating of the mixture is carried out at a temperature comprised between 80 and 180 °C during 1 to 6 hours.
- An aroma product according to claim 6, wherein the heating of the mixture is carried out at a temperature of 100
 - The use of the aroma product according to any of claims 1 to 7, wherein 0.1 to 5 % of the aroma product is mixed with a food taken in the group consisting of bouillons, soup, sauces, gravies, petfood, snacks and canned food.

55



EUROPEAN SEARCH REPORT

Application Number EP 98 12 3554

	DOCUMENTS CONSIDE Citation of document with indi	Relevant	CLASSIFICATION OF THE	
Category	Citation of document with incl of relevant passag	es	to daim	APPLICATION (Int.Cl.5)
X	WO 94 07377 A (UNILE (NL)) 14 April 1994 * examples I-V *	VER PLC ;UNILEVER NV	1,2,8	A23L1/035 A23L1/22 A23L1/227 A23L1/231
X	WO 92 09209 A (UNILE (NL)) 11 June 1992	VER PLC ;UNILEVER NV	1,2,8	7.2022, 201
Y	* example IV *		1-8	
X	E. BOYLE: "Monoglyc Systems: Current and FOOD TECHNOLOGY, vol. 51, no. 8, - 1 XPO00697936	1,8		
Y	* page 58 *		1-8	
Y	EP 0 486 822 A (NEST * column 1, line 8 - * page 2, line 23 -	7 1-8		
Y	MUELLER U., BAUCH A. extrahieren" LEBENSMITTELTECHNIK. vol. 29, no. 5, - 1 XP002104303 * page 49 *	.: "Mit Emulgatoren	1-8	TECHNICAL FIELDS SEARCHED (IM.CH.6) A23L
			_	
	The present search report has			Exeminer
	Pigge of scarch	Date of completion of the sear		Bendl, E
X:F	MUNICH CATEGORY OF CITED DOCUMENTS	E : earlier pate after the fill	rinciple underlying ant document, but ing date	the invention published on, or
X S	sarticutarly relevant if taken alone sarticularly relevant if combined with and locument of the same category achnological background	cited in the applica cited for other reas	atlon cons	

ANNEX TO THE EUROPEAN SEARCH REPORT ON EUROPEAN PATENT APPLICATION NO.

EP 98 12 3554

This annex lists the patent family members relating to the patent documents cited in the above-mentioned European search report. The members are as contained in the European Patent Office EDP file on The European Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

31-05-1999

Patent document cited in search report		Publication date		Publication date	
WO 9407377	Α	14-04-1994	AT	169183 T	15-08-19
			AU	672031 B	19-09-19
			AU	4818993 A	26-04-19
			CA	2145536 A,C	14-04-19
			CZ	9500772 A	17-01-19
•			DE	69320213 D	10-09-19
		•	DE	69320213 T	18-02-19
			EP	0777424 A	11-06-19
			HU	71772 A	29-01-19
			PL	308206 A	24-07-19
			SK	39695 A	11-07-19
			ÜS	5620734 A	15-04-19
			ZA	9307188 A	
					28-03-19
WO 9209209	A	11-06-1992	AT	108306 T	15-07-19
			AU	663061 B	28-09-19
			AU	8863291 A	25-06-199
			CA	2082543 A	13-05-19
•			CA	2096429 A	24-05-19
			DE	69102885 D	18-08-19
			DE	69102885 T	10-11-19
			DK	558523 T	28-11-199
			EP	0558523 A	08-09-199
			ES	2056665 T	01-10-199
			FI	932290 A	24-06-199
			GR	3025710 T	31-03-199
			ΙE	65342 B	18-10-199
			JP	2620989 B	18-06-199
			JP Kr	6502530 T	24-03-199
		·		126819 B	26-12-199
			NZ Pt	240627 A	22-12-199
			TR	99588 A 26436 A	30-10-199
			ÜS	5652011 A	15-03-199
,			ZA	9109231 A	29-07-199
				7103231 A	21-05-199
EP 0486822	A	27-05-1992	US	5039543 A	13-08-199
			AT	99130 T	15-01-199
			AU	638391 B	24-06-199
		•	AU	8682791 A	21-05-199
			CA	2055278 A	17-05-199
			DE	69100894 D	10-02-199
			DE	69100894 T	11-05-199
			DK	486822 T	25-04-199
			ES	2049070 T	01-04-199
•			FI	915376 A	17-05-199
 		ficial Journal of the Europe			

ANNEX TO THE EUROPEAN SEARCH REPORT ON EUROPEAN PATENT APPLICATION NO.

EP 98 12 3554

This annex lists the patent family members relating to the patent documents cited in the above-mentioned European search report. The members are as contained in the European Patent Office EDP file on The European Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

31-05-1999

F	Patent document ad in search repo	ort	Publication date	Publication Patent family date member(s)			Publication date	
EP	0486822	A		JP PT	4304863 99507	A A	28-10-1992 29-01-1993	
•								

o will be annown in the European Patent Office, No. 12/82

•) _{vi} . .

INTERNATIONAL SEARCH REPORT

1. R.

International Application No

			101/EF 02/	10031			
A. CLASSII IPC 7	FICATION OF SUBJECT MATTER A23L1/035 A23G1/00						
According to	International Patent Classification (IPC) or to both national classific	cation and IPC					
	SEARCHED						
Minimum do IPC 7	cumentation searched (classification system followed by classification sys	tion symbols)					
	ion searched other than minimum documentation to the extent that			urched			
	ata base consulted during the international search (name of data b	ase and, where practical,	search terms used)				
C. DOCUME	ENTS CONSIDERED TO BE RELEVANT						
Category °	Citation of document, with indication, where appropriate, of the re	elevant passages		Relevant to claim No.			
A	EP 1 008 305 A (NESTLE SA) 14 June 2000 (2000-06-14) the whole document			1-5			
	•	•		·			
			!				
<u>.</u> :				·			
		•					
Furti	her documents are listed in the continuation of box C.	X Patent family	members are listed	in annex.			
1	ategories of cited documents :		d not in conflict with	the application but			
consid	ent defining the general state of the art which is not dered to be of particular relevance document but published on or after the international tate	invention "X" document of partic	nd the principle or the	laimed invention			
"L" docume which citatio	ent which may throw doubts on priority claim(s) or is cited to establish the publication date of another n or other special reason (as specified)	involve an inventi "Y" document of partic cannot be conside	cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the				
P docume	ent referring to an oral disclosure, use, exhibition or means ent published prior to the international filing date but han the priority date claimed	document is combined with one or more other such documents, such combination being obvious to a person skilled in the art. *8* document member of the same patent family					
	actual completion of the international search		the international sea				
2	O January 2003	27/01/2	2003				
Name and i	mailing address of the ISA European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk	Authorized officer					
	Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Fax: (+31-70) 340-3016	Weber,	G				

2

M. 3